

Supporting information for

**The Co d-band center modulation of LaCoO_{3-δ} for improved
peroxymonosulfate activation**

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Text S1. Chemicals

Bisphenol A (BPA, 99.8%), lanthanum nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.99%), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99.99%), ammonium biphosphate ($\text{NH}_4\text{H}_2\text{PO}_4$, 99.99%), tert-butyl alcohol (TBA, 99.5%), citric acid (99.5%), Ethylenediaminetetraacetic acid (EDTA, 99.5%), ammonia solution (25%), anhydrous sodium sulfate (Na_2SO_4 , 98%), humic acid (HA), sodium chloride (NaCl, 99.5%), sodium dihydrogen phosphate (NaH_2PO_4 , 99.0%), sodium bicarbonate (NaHCO_3 , 99.5%), sodium phosphate dibasic (Na_2HPO_4 , 99.0%), potassium iodide (KI, 99.99%), deuterioxide (D_2O , 99.9%), methanol (99.8%) and sodium hydroxide (NaOH, $\geq 98\%$) were purchased from Aladdin. 5,5-Dimethyl-1-pyrroline N-oxide (DMPO, $\geq 98\%$) was obtained from Sigma-Aldrich. Potassium peroxymonosulfate (KHSO_5 , $\geq 98\%$), furfuryl alcohol (FFA, 98%), p-benzoquinone (p-BQ, 97%), and 2,2,6,6-tetramethyl-4-piperidinol (TMP, 99%) were purchased from Macklin. Hydrochloric acid (HCl, 36%) was bought from Guangzhou Chemical Reagent Factory. All the chemicals were used directly without further purification.

Text S2. The procedures of NH_3 -TPD, CO_2 -TPD, and H_2 -TPR

Temperature-programmed desorption and reduction were performed on an AutoChem1 II 2920 instrument. For NH_3 -TPD, the catalyst (50–100 mg) was preheated at 300 °C at a heating speed of 10 °C/min and purged with He flow (30 mL/min) for 1 h. After cooling to 30 °C, an NH_3 /He mixture (30 mL/min) was fed in for 1 h until saturation. Then the weak physically adsorbed NH_3 on the surface was removed by He flow purge for 1 h. Finally, the NH_3 was desorbed and detected at 800 °C in He atmosphere at a heating rate of 10 °C/min.

For CO_2 -TPD, the catalyst (100 mg) was preheated at 300 °C at a heating speed of 10 °C/min and purged with He flow (50 mL/min) for 2 h. After cooling to 100 °C, ventilate the CO_2 (50 mL/min) for 1h, and switch over the He airflow (50 mL/min) to purge for 1h. After dropping to room temperature and leveling the baseline, the sample rose to 800 °C at 10 °C/min, and the flowing gas was detected by TCD.

For H_2 -TPR, the catalyst was dried at 500 °C for 2 h at a heating rate of 10 °C/min, swept by a He flow (50 mL/min). After cooling to room temperature, a 10% H_2 /Ar

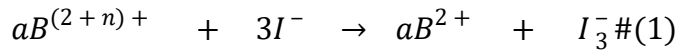
mixture (50 mL/min) was provided for 30 min. After the baseline got stable, the sample was treated at 800 °C in the 10% H₂/Ar mixture with a heating rate of 10 °C/ min.

Text S3. The iodometric titration experiments

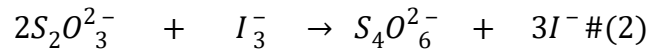
The catalysts (0.01 g) and KI powder (0.03 g) were mixed in a cone bottle and dissolved by diluted hydrochloric acid (~18%). Then a certain amount of starch solution was added to the dissolved solution above, and titration was initiated using Na₂S₂O₃ solution (0.01 mol/L).

The δ value was calculated as follows:

Reaction:



$$\frac{m}{M_0} = \frac{1}{a} \times \frac{m}{M_0}$$



$$\frac{2}{a} \times \frac{m}{M_0} = \frac{1}{a} \times \frac{m}{M_0}$$

Calculation:

$$a \times (2 + n) - 3 = a \times 2 - 1 \quad \text{charge balance of reaction (1)}$$

$$a = \frac{2}{n}$$

$$2 \times (3 - \delta) = 3 + 2 + n \quad \text{charge balance of LCO (2)}$$

$$2 \times (3 - \delta) = 3 + (2 + n) \times 0.8 + 3 \times 0.2 \quad \text{charge balance of LC}_{0.8}\text{P}_{0.2}\text{O (2)}$$

$$\delta(LCO) = \frac{1 - n}{2} \quad \delta(LC_{0.8}P_{0.2}O) = 0.4 - 0.4n$$

$$C(Na_2S_2O_3) \times V(Na_2S_2O_3) = \frac{2}{a} \times \frac{m}{M_0} \quad \text{molar balance of reaction (1) and (2)}$$

$$\text{So, } \delta(LCO) = 0.5 - \frac{M_0 CV}{2m} \quad \delta(LC_{0.8}P_{0.2}O) = 0.4 - \frac{0.4M_0 CV}{m}$$

m: the weight of perovskite powder

M₀: the molecular weight of catalysts (LCO, LC_{0.8}P_{0.2}O)

C: the molarity of Na₂S₂O₃

V: the volume of $\text{Na}_2\text{S}_2\text{O}_3$ used for titration

Text S4. The concentration testing of the PMS

The solution containing NaHCO_3 (1.2 g/L) and KI (4.98 g/L) was prepared. At a given time interval, 0.1 mL of the reaction solution was extracted and filtered with a film (0.45 μm). Then the clear liquid was injected into 4.9 mL of the NaHCO_3/KI solution. After shaking for a while, the samples were tested with an ultraviolet and visible (UV-vis) spectrophotometer.

Text S5. The electrochemical tests

The i-t curves were obtained at a CHI760E electrochemical workstation. A standard three-electrode electrochemical cell assembly includes a reference electrode (Ag/AgCl), a counter electrode (platinum sheet), and a working electrode. The working electrode is covered with 20 μL of catalyst ink which was prepared as follows: 5 mg of catalyst powder, 5 mg of conductive carbon black, 1 mL of isopropanol, 0.5 mL of Nafion (0.5 wt.%) were mixed and sonicated until forming a uniform ink. The i-t tests were performed at 0.00 V *vs.* Ag/AgCl in the Na_2SO_4 electrolyte (50 mM). After the first 200 s, PMS was added into the electrolyte, and BPA was subsequently joined in the $\text{Na}_2\text{SO}_4/\text{PMS}$ solution after 400 s.

Table S1. The oxygen components on the surface of LCO and $\text{LC}_{0.8}\text{P}_{0.2}\text{O}$.

Samples	LCO	$\text{LC}_{0.8}\text{P}_{0.2}\text{O}$
M-O	40.35%	28.09%
O_V	53.29%	65.34%
$\text{H}_2\text{O}/\text{CO}_2$	6.37%	6.56%

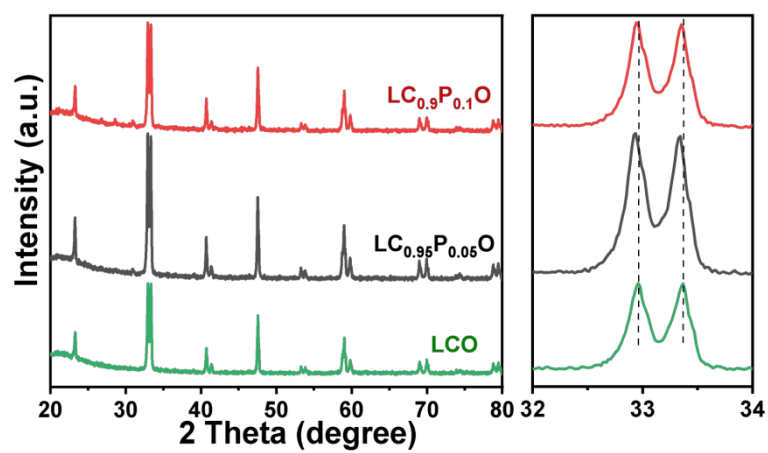


Fig. S1 XRD patterns of LCO, $\text{LC}_{0.95}\text{P}_{0.05}\text{O}$ and $\text{LC}_{0.9}\text{P}_{0.1}\text{O}$.

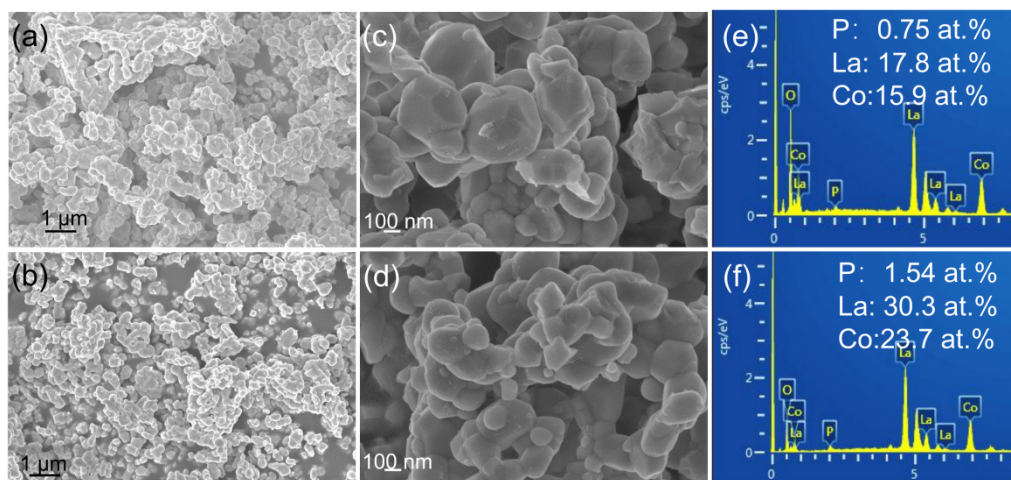


Fig. S2 SEM images (a-d) and EDS spectra (e and f) of $\text{LC}_{0.95}\text{P}_{0.05}\text{O}$ (a, c, e) and $\text{LC}_{0.9}\text{P}_{0.1}\text{O}$ (b, d, f).

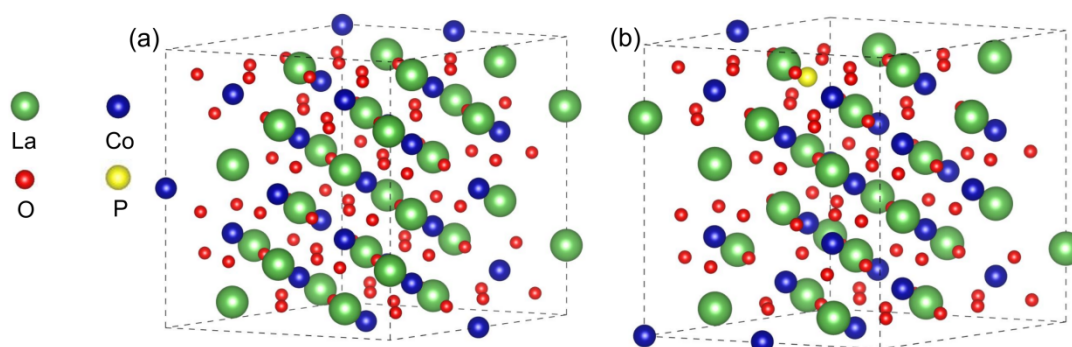


Fig. S3 Crystal structures of LCO (a) and P-LCO (b) after structural optimization.

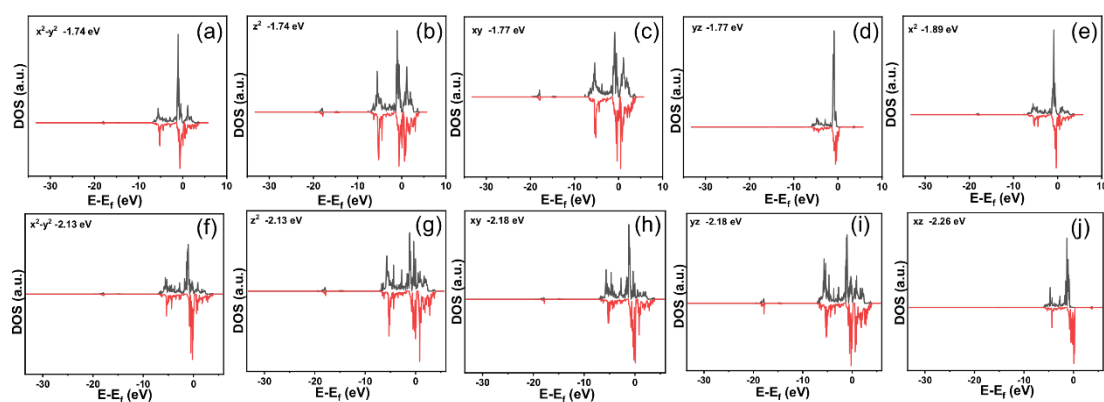


Fig. S4 The DOS of suborbitals of P-LCO (a–e) and LCO (f–j).

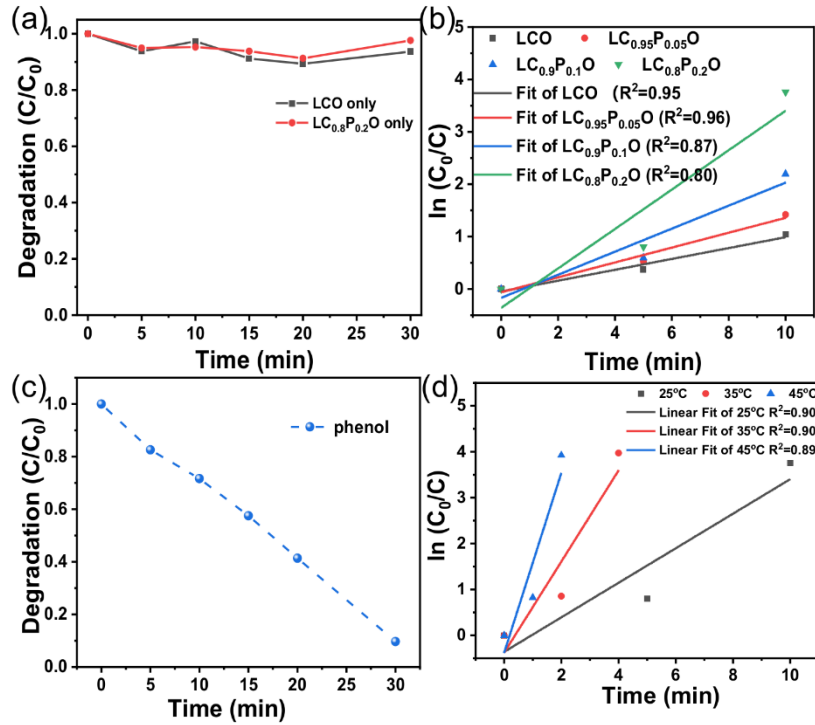


Fig. S5 The adsorption of LCO and LC_{0.8}P_{0.2}O (a), fitting lines and reaction kinetics of the catalysts (b), the catalytic degradation of phenol (c) and fitting lines at different reaction temperatures (d) on LC_{0.8}P_{0.2}O. Reaction conditions: [catalysts] = 0.1 g/L, [PMS] = 3.25 mM, [phenol] = 20 ppm, T = 25 °C.

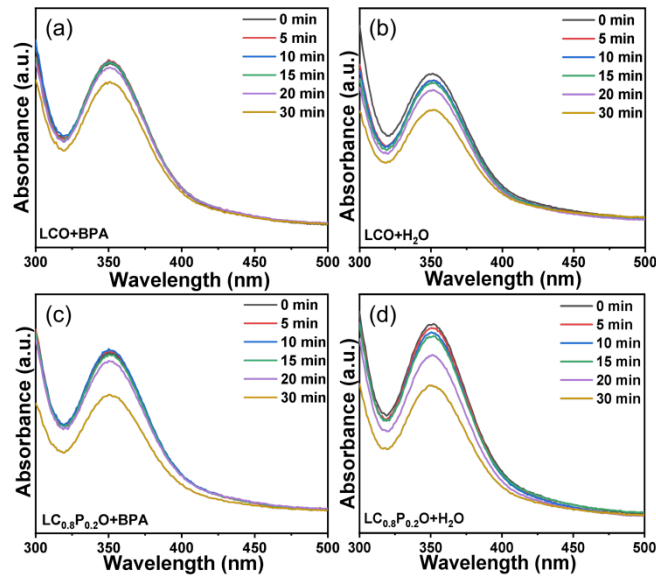


Fig. S6 The UV-vis spectra of PMS under different reaction conditions. Reaction conditions: [Initial PMS] = 3.25 mM, [BPA] = 20 ppm, T = 25 °C

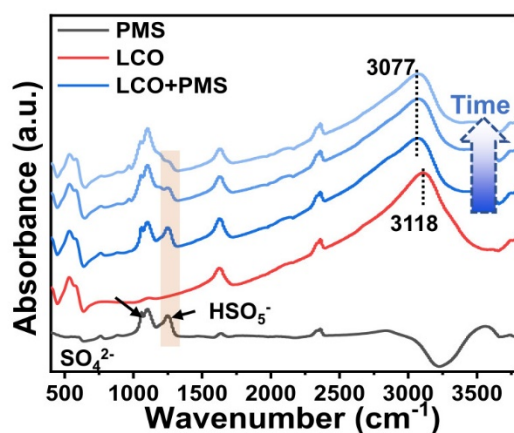


Fig. S7 The ATR-FTIR spectra of LCO/PMS system.

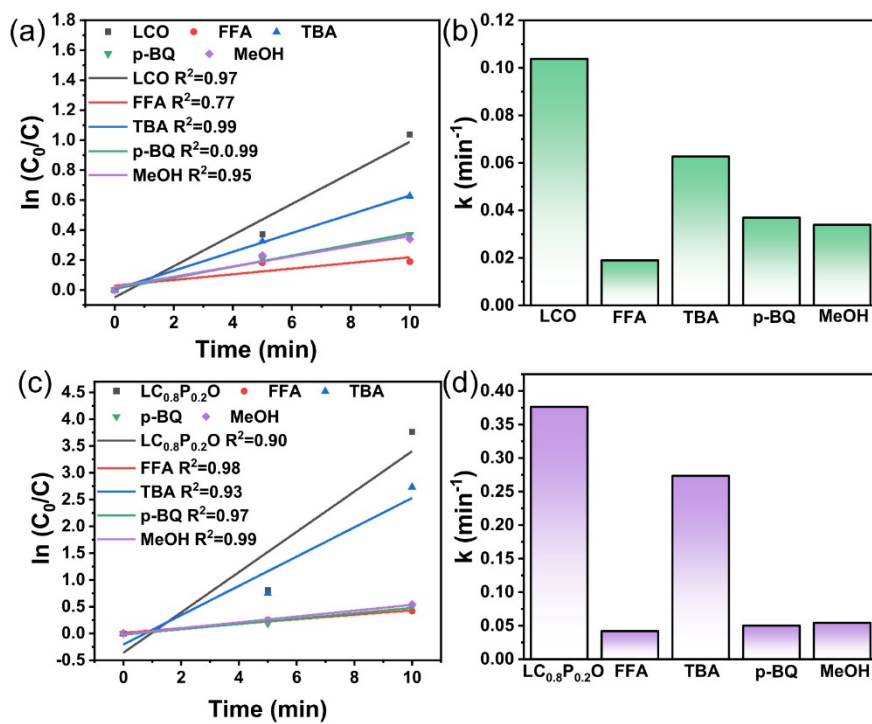


Fig. S8 The first-order reaction kinetic fitting (a, c) and rates (b, d) of quenching results for LCO (a, b) and $\text{LC}_{0.8}\text{P}_{0.2}\text{O}$ (c, d).